GAS TECHNOLOGY INSTITUTE

Gas to Liquids: Technical Challenges

Dane A. Boysen, PhD

Executive Director, Research Operations
Gas Technology Institute

Chemical Conversion via Modular Manufacturing:
Distributed, Stranded, and Waste Feedstocks

St. Louis MO, December 4, 2015

Company History

more than half a century in gas research

1940 1950 1960 1970 1980 1990 2000 2010

1941

Institute for Gas Technology (IGT) formed at the Illinois Institute of Technology (IIT)

1947 IGT Laboratory
Chicago, Illinois

1970 Blue Flame natural gas powered rocket car sets world land speed record of 630 mph

1973

Oil Crisis

1970 HYGAS® Pilot Plant
Chicago, Illinois

1976

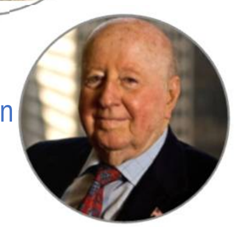
Federal Power Commission approved surcharge on pipeline transmission for research funding and Gas Research Institute (GRI) formed

Dr. Henry Linden
GRI President

Dr. James L. Johnson
Pioneer in Coal Gasification

1991

GRI sponsors Mitchell Energy's first horizontal well in the Barnett shale



George Mitchell

1992

FERC Order No. 636, Restructuring Rule mandated unbundling to separate sales from transportation services

1995 U-GAS® Plant
Shanghai, China

2000

GRI and IGT combined to form the Gas Technology Institute (GTI)

2009 GTI Advanced Gasification Facility
Des Plaines, Illinois

Workshop Discussion Topics

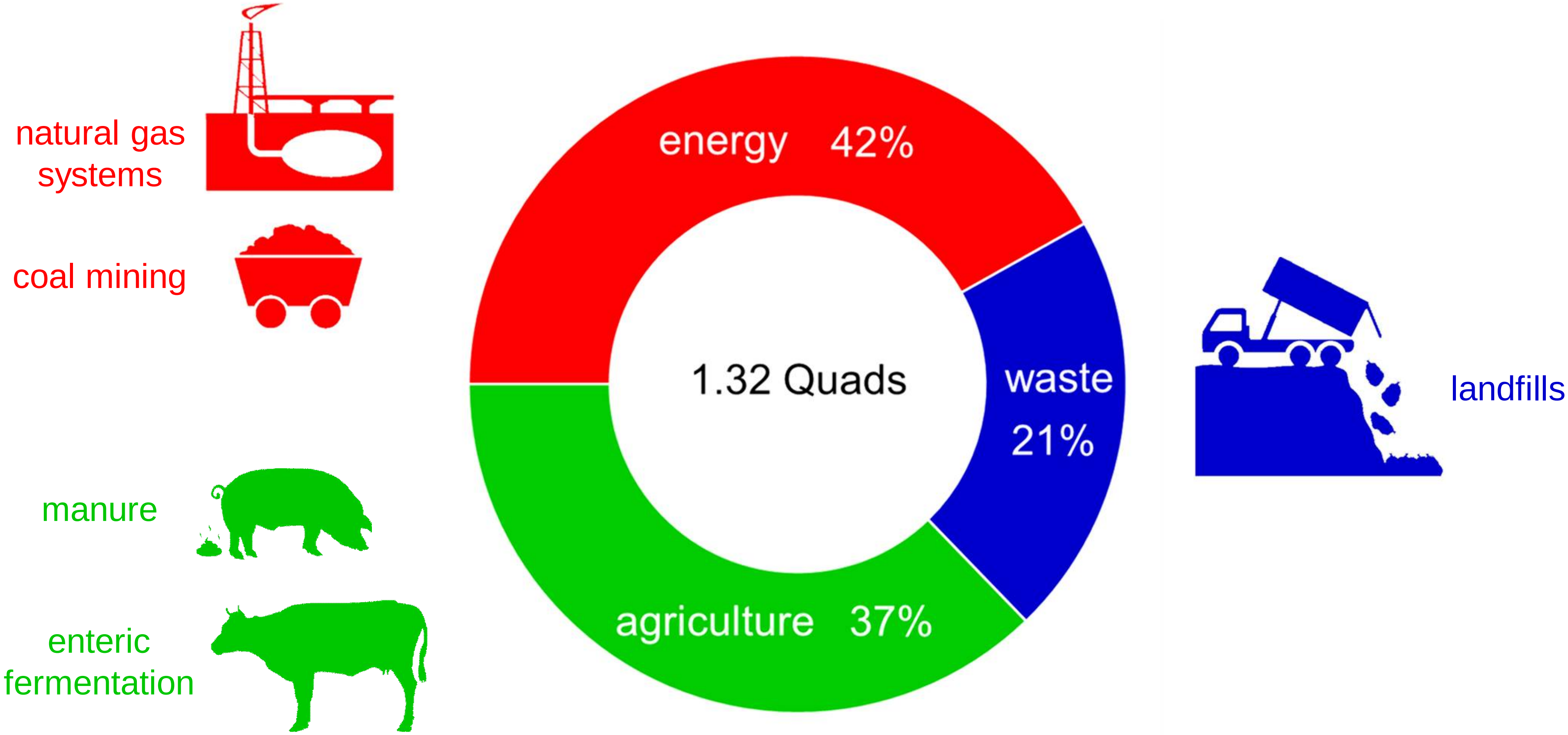
1. Why this technology would work for conversion at modular scale
2. Barriers to technology
3. Technical holes that national labs and universities should focus on
4. Barriers to implementation
5. Commonalities to barriers
6. Best approaches

Roadmap

1. The Problem
2. The Challenge
3. The Opportunity

What is the problem we are trying to solve?

2013 U.S. Anthropogenic Methane Emissions



Source: U.S. EPA Inventories of U.S. Greenhouse Gas Emissions and Sinks: 1990-2013. http://www3.epa.gov/climatechange/ghgemissions/usinventoryreport.html#fullreport

U.S. Methane Emissions 2013

Methane has 23-86 times the global warming potential of carbon dioxide

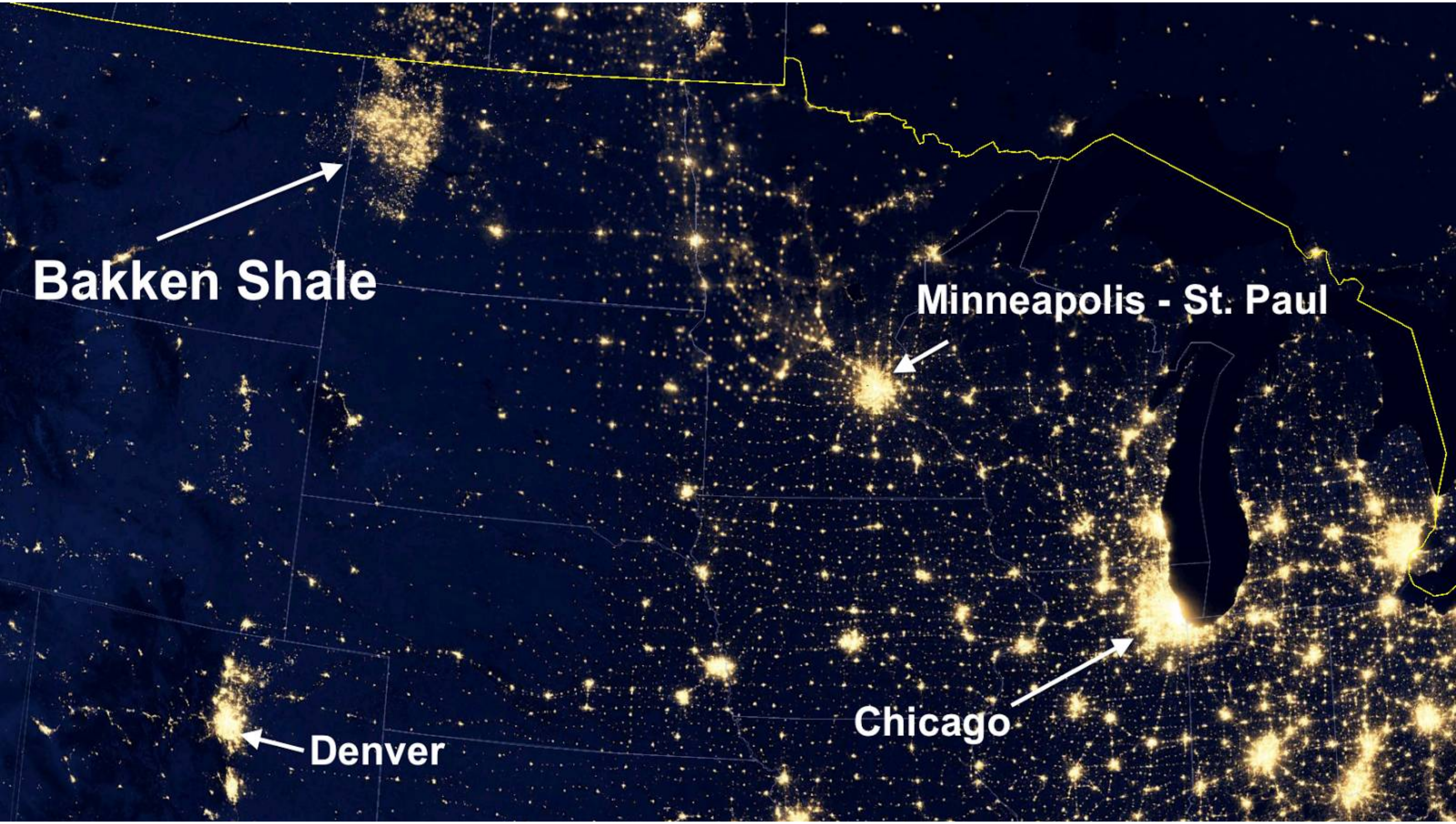
~ 630 $Mt_{CO2,eq}$

~ 10% of total GHGs

~ 1.3 Quads of energy

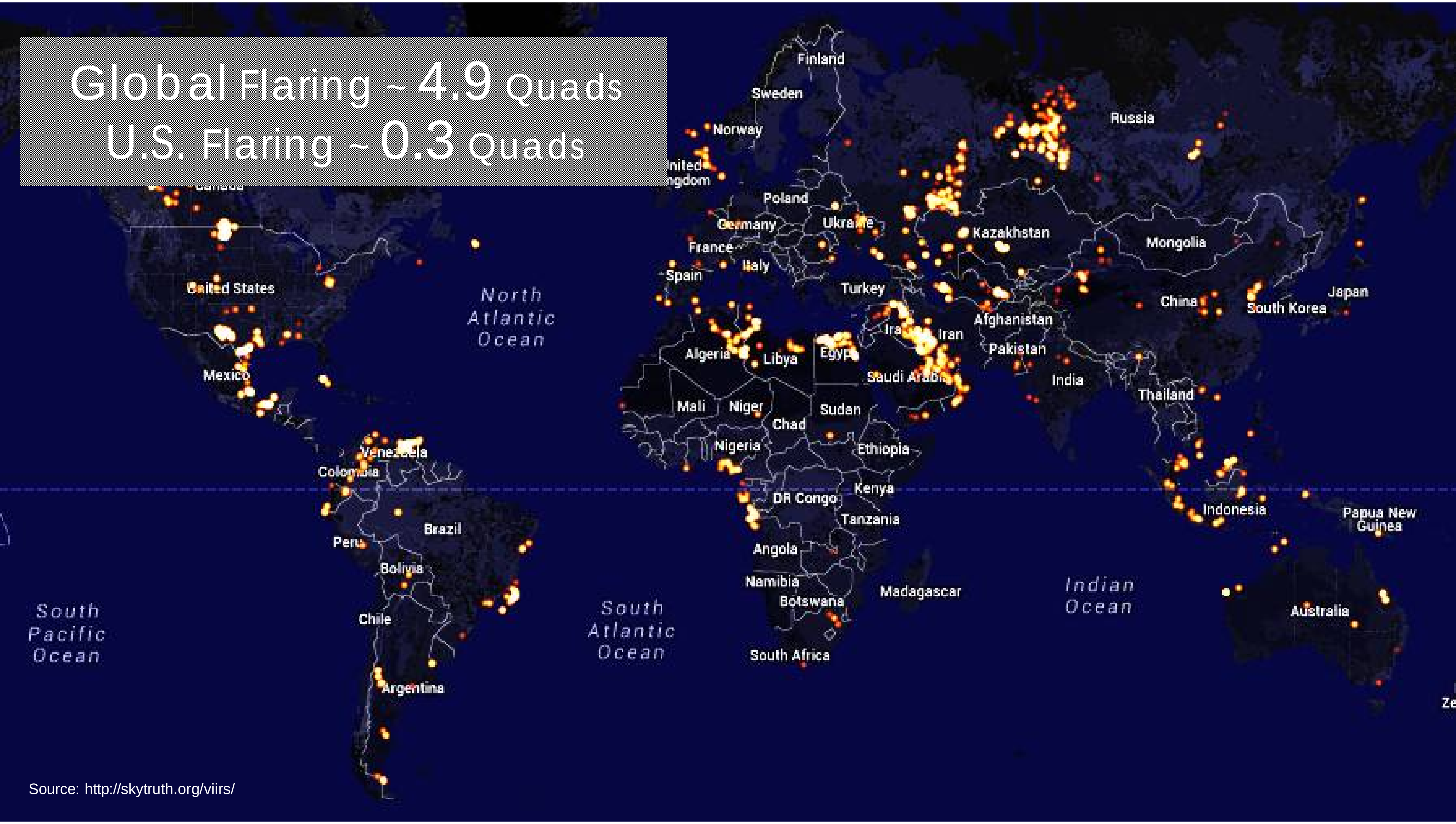
Source: U.S. EPA Inventories of U.S. Greenhouse Gas Emissions and Sinks: 1990-2013. http://www3.epa.gov/climatechange/ghgemissions/usinventoryreport.html#fullreport


Can you guess this city?
Minneapolis St. Paul
Chicago
Denver
Kansas City
St. Louis
Credit: NASA Earth Observatory/NOAA NGDC


Bakken Shale
Minneapolis - St. Paul
Chicago
Denver

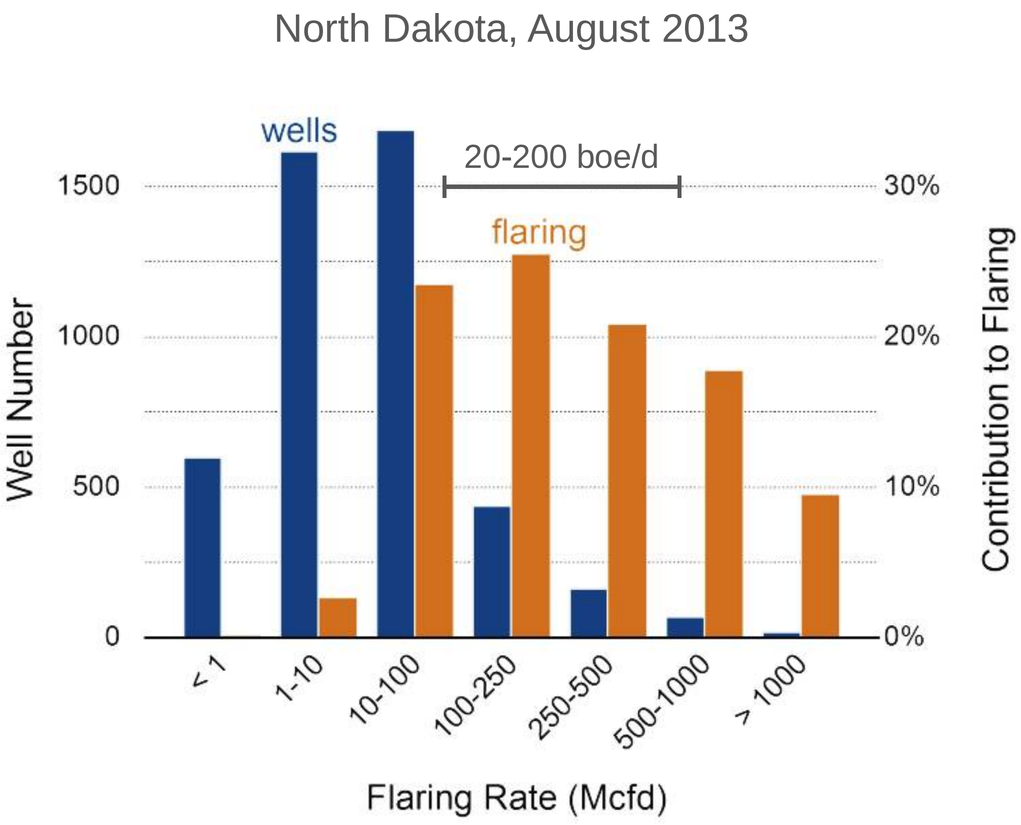
Global Flaring ~ 4.9 Quads

U.S. Flaring ~ 0.3 Quads



Source: http://skytruth.org/viirs/

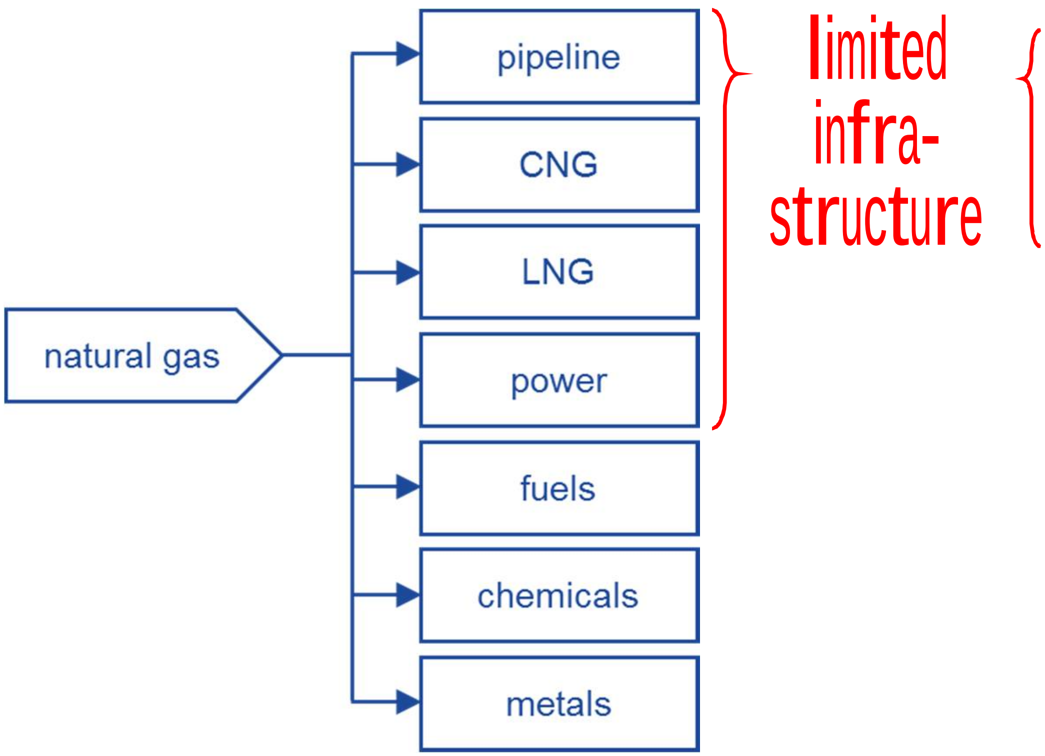
Most U.S. flares come from small wells



To address gas flaring, propose solutions should scale down to ~ 300 mcf/d natural gas input (50 boe/d)

needs deeper analysis

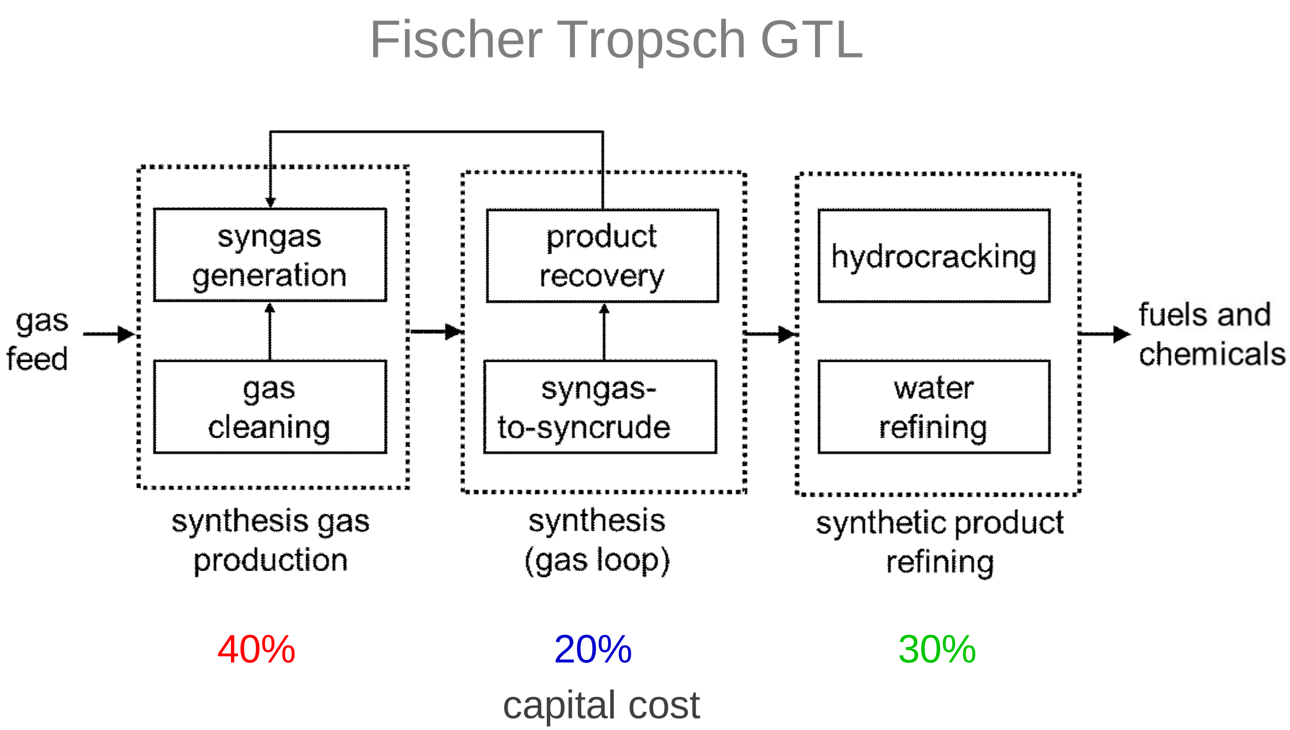
Natural Gas Monetization Options

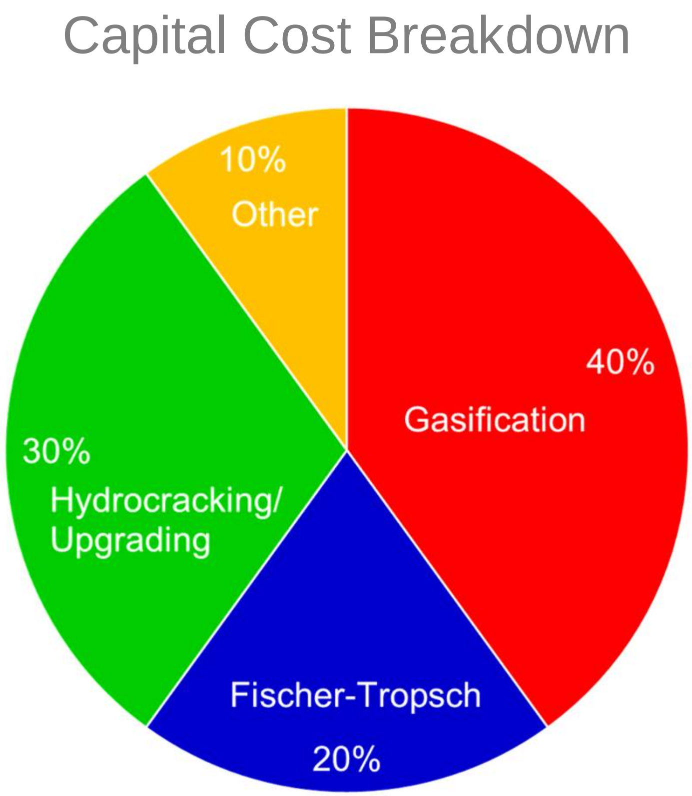


Product	($/t)	($/L)	($/boe)*
Natural Gas	110	0.00007	12
Electricity	—	—	20
CNG	375	0.07	41
LNG	467	0.21	51
Methanol	366	0.29	100
Ammonia	540	0.37	147
Diesel	535	0.41	69
Gasoline	740	0.50	94
Jet Fuel	846	0.62	108
Ethanol	862	0.68	177
Ethylene	1292	0.73	159
Propylene	1367	0.84	171
Benzene	1303	1.14	190
Aluminum	1442	3.89	283

*based on combustion enthalpies

Commercial Fischer Tropsch GTL





Gas-To-Liquid Economics

GTL Facility	Company	Capacity	Capital Cost[3]
Pearl	Shell	140,000 bpd[1]	~ $110,000/bpd
Escravos	Sasol-Chevron	33,000 bpd[2]	~ $180,000/bpd
Sasol I expansion	Sasol	---	~ $200,000/bpd

bpd = barrels per day
boe = barrels of oil equivalent

- Simple payback = $150,000/bpd ÷ $50/boe ~ 8 years
- FT-GTL is not economically attractive at current market prices

Sources: (1) A. de Klerk. Gas-to-liquid conversion. ARPA-E natural gas conversion technologies workshop. Houston TX, Jan 13, 2012. (2) Pearl GTL - an overview. Shell, 2012. http://www.shell.com/home/content/aboutshell/our_strategy/major_projects_2/pearl/overview/ (3) B. Reddall. Cost of delayed Chevron Nigeria plant now $8.4 bln. Thomson Reuters. 24 Feb 2011.

GTL Plant – you can see it from space

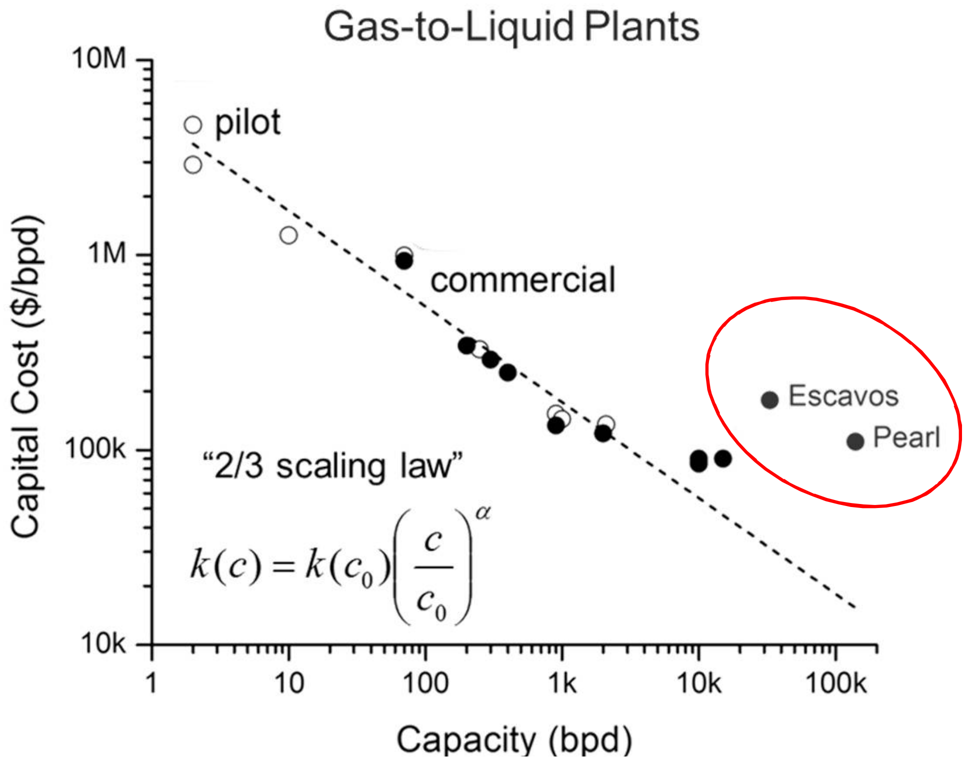
price tag ~ $15 billion

Shell Pearl GTL Facility, Qatar

Source: E.W. Merrow. Understanding the outcomes of megaprojects: a quantitative analysis of very large civilian projects, The RAND Corporation, Santa Monica, CA, 1988.

Current Paradigm

economies of unit scale



Sources: (1) PJA Tijm. Gas to liquids, Fischer-Tropsch, advanced energy technology, future's pathway. Feb 2010; (2) C. Kopp. The US Air Force Synthetic Fuels Program. Technical Report APA-TR-2008-0102. (2008)

The Problem

1. About 1.6 Quads and 10% GHG emissions result from flared or vented methane in U.S.
2. Emissions fundamentally distributed in nature
3. Existing large scale gas-to-liquid solutions cannot address this problem

Roadmap

1. The Problem
2. The Challenge
3. The Opportunity

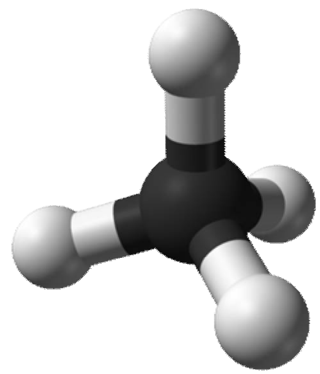
What are the fundamental challenges?

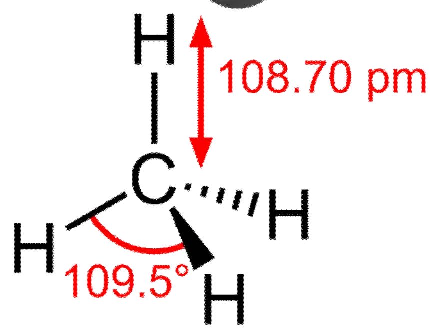
Methane - the MC Hammer of molecules

Methane activation is difficult because chemical attack inhibited by

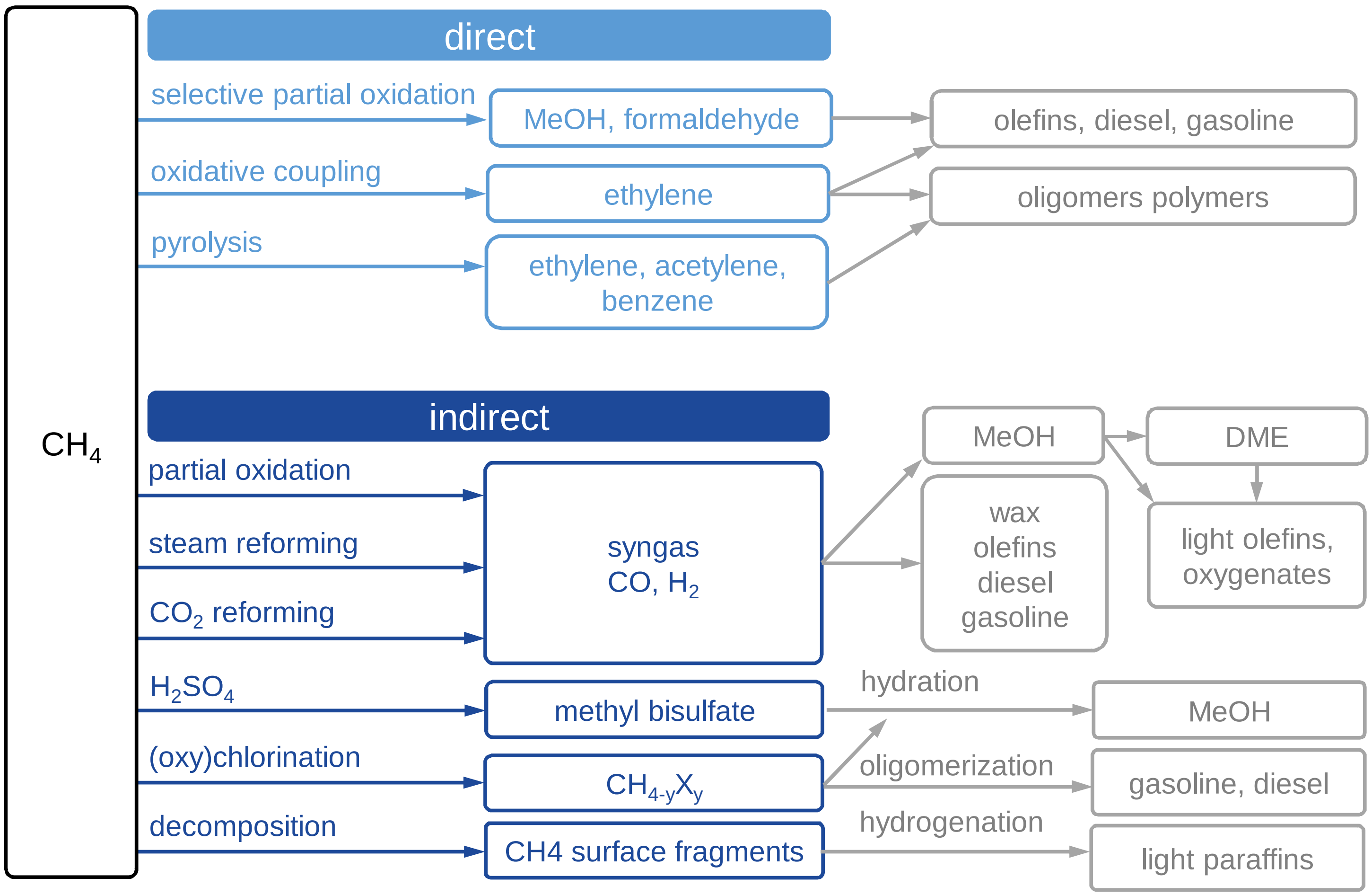
- Strong tetrahedral bonds
- No functional groups
- No magnetic moment
- No polar distribution

Bond	E / kJ mol^{-1}
$H_3C{-}H$	439
$H_3C{-}CH_3$	350
$H_3C{-}OH$	381





Methane routes to fuels and chemicals



Basic challenges

Direct routes $CH_4 \xrightarrow{cat} -[CH_n]- \rightarrow \times C$

- Overcome thermodynamic constraints
- Protect weaker C-bonds in products
- Inhibit carbon formation

Bond	E / kJ mol^{-1}
H_3C-H	439
H_3C-CH_3	350
H_3C-OH	381

Basic challenges

Direct routes $CH_4 \xrightarrow{cat} -[CH_n]- \longrightarrow\!\!\times\, C$

- Overcome thermodynamic constraints
- Protect weaker C-bonds in products
- Inhibit carbon formation

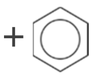
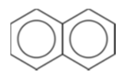
Bond	E / kJ mol^{-1}
$H_3C{-}H$	439
$H_3C{-}CH_3$	350
$H_3C{-}OH$	381

Indirect routes $CH_4 \xrightarrow{cat} I_1 \longrightarrow I_2 \longrightarrow -[CH_n]-$

- Inhibit carbon formation
- Use less costly oxidants
- Couple exothermic-endothermic steps
- Form first C-C bond

example: $I_1 = H_2, CO$
$I_2 = CH_3OH$

Direct conversions

Direct Route	Chemistry	Challenge
Non-oxidative conversion (pyrolysis)	$CH_4 \leftrightarrow H_2 + C_2H_4$ $\leftrightarrow H_2 +$  $\leftrightarrow H_2 +$  $\leftrightarrow H_2 + C$ (Mo/ZSM5)	▪ Thermodynamically uphill ▪ Thermo equil < 12% at 700°C ▪ Coke formation ▪ Catalyst de-activation
Oxidative coupling	$CH_4 \xrightarrow{k_1} C_2H_{4,6}$ $CH_4 \xrightarrow{k_2} CO_n$, $C_2H_{4,6} \xrightarrow{k_3} CO_n$ (O_2) (Na_2WO_4/SiO_2)	▪ Combustion reaction ($k_3 > k_1$) ▪ Low yield (< 25%)
Partial oxidation	$CH_4 + O_2 \rightarrow CH_3OH$ $\rightarrow CH_2O$ (Mo/SiO_2)	▪ Formaldehyde bi-product ▪ Low yield (< 10%)

Indirect conversions

How do we activate first C-bond and protect is from going back to a C-H bond?

$CH_4 \xrightarrow{O_2, H_2O} H_2, CO$		thermodynamic
$\xrightarrow{Br_2} CH_3Br$		kinetic
$\xrightarrow{H_2SO_4} CH_3OSO_3H$		kinetic

- Use “protected” form of methane as intermediate
- Minimize cost of oxidants

Indirect conversions

Steam reforming:	$CH_4 + H_2O \rightarrow CO + 3H_2$ ✓	3:1 H_2/C ✗
Partial oxidation:	$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$ ✗	2:1 H_2/C ✓
Fischer-Tropsch:	$CO + 2H_2 \rightarrow -(CH_2)- + 2H_2O$	2:1 H_2/C

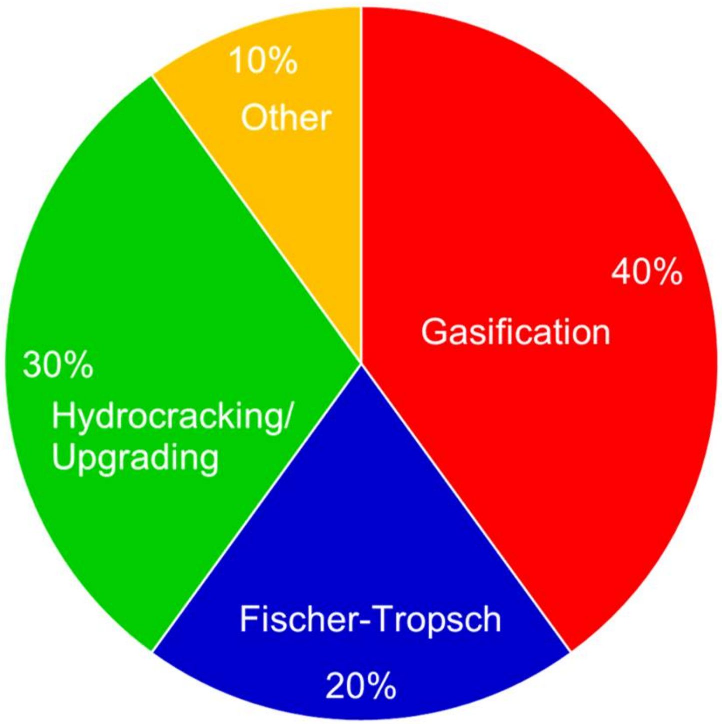
Key Questions:

(1) Is the H_2/C ratio matched?

(2) Is the oxidant inexpensive?

Critical: must have a low cost oxidant

Fischer Tropsch GTL
Capital Cost Breakdown



In GTL facility about 30% capex due to cryogenic air separation and utilities for gasification

Source: (1) Zennaro, R. In Greener Fischer-Tropsch processes, Maitlis, P., De Klerk, A. Eds.; Wiley-VCH (to be published), (2) Dry, M. E.; Steynberg, A. P. Stud. Surf. Sci. Catal. 2004, 152, 406-481 (p.442).

gti

The Challenge

1. Identify a direct conversion pathway to make first C-C bond without adding process complexity

   or

2. Find a low cost non-oxygen oxidant that will activate methane C-bond and protect until first C-C bond formed

   or

3. Develop low cost oxygen separation from air at small scale (O_2 < \$20/t)

Roadmap

1. The Problem
2. The Challenge
3. The Opportunity

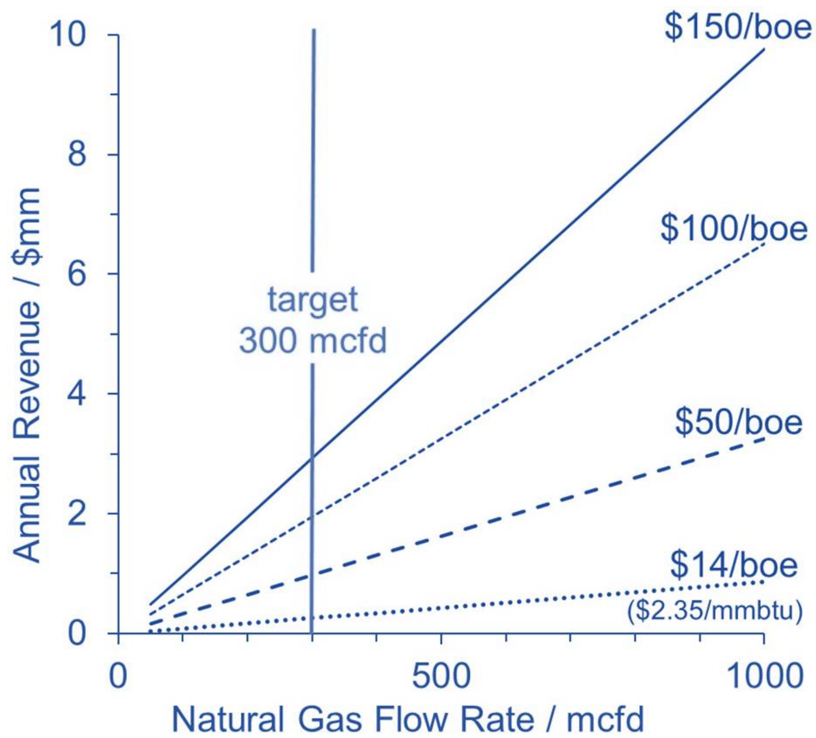
Proposed Optimal Modular Capacity

Resources

- Flared gas
- Vented gas
- Coal
- Biomass

Feedstock	Feed Rate
Natural Gas	300 Mcf/d
	300 MMBtu/d
	52 boe/d
	316 GJ/d
	3.7 MW_{th}
Wood	18 t/d
Coal	10 t/d

Sanity Check – is there a market here?

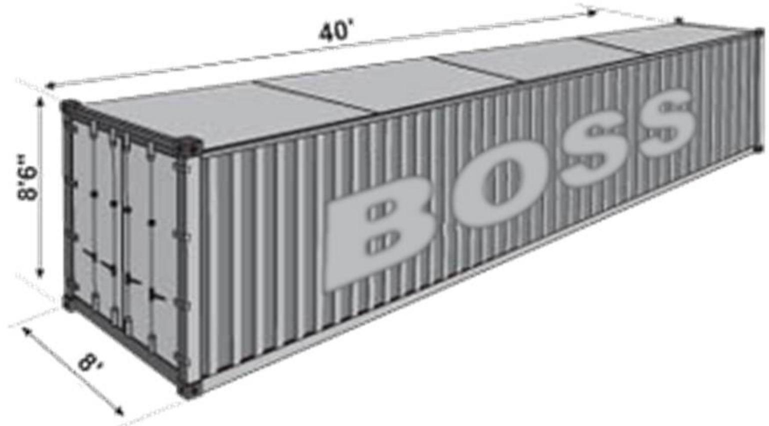


		U.S.	World
Unit Capacity	mcf/d	300	300
Flaring Rate	bcf/y	289	4940
Modular Units	ea	2,640	45,200
Product value	$/boe	100	100
Unit Revenue	$/y	1.89M	1.89M
Capital Cost	$/unit	5.66M	5.66M
Total Available Market	$bn	15	256

*CapEx = 3x revenue

Reality Check – shipping containers, really?

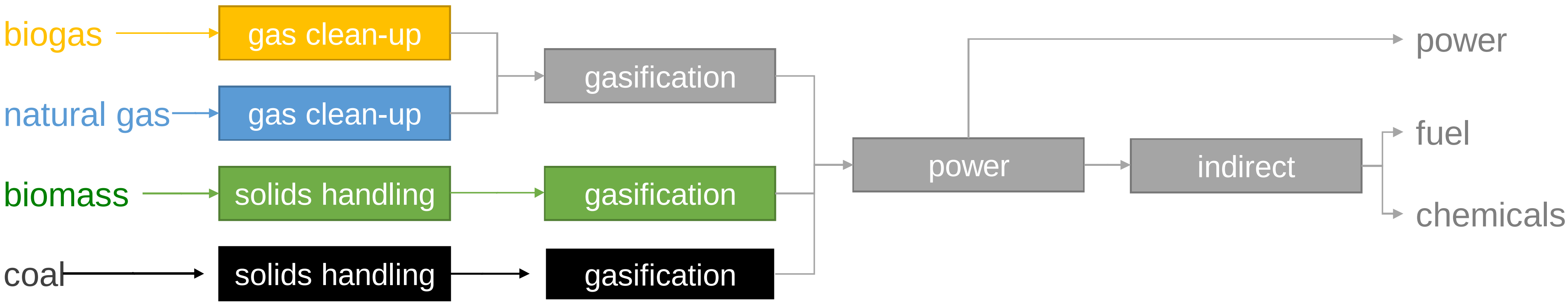
Gas feed rate	300 mcf/d
Packing Efficiency	20%
Reactor Volume	477 cf
Space Velocity	26 h^{-1}



Length	40	ft	12.192	m
Width	8	ft	2.438	m
Height	8.5	ft	2.591	m
Internal Volume	2,385	cf	67.5	m^3
Maximum Weight	66,139	lb	30,400	kg
Empty Weight	8,380	lb	3,800	kg

What is the big opportunity?

Modular Vision



Modular Architecture

- Standard interfaces
- Common feed rates and compositions
- Inter-module design standard
- Plug and play protocol

Modular Platform

- Common component inventories
- Intra-module design standard
- Uniform form factor

Technologies that democratized the world

1450	1908	1973	1977	????
Gutenburg Press	Ford Model T	Motorola DynaTAC 8000X	Commodore PET	Modular Processing
information	**transportation**	**communication**	**computation**	**processing**

GAS TECHNOLOGY INSTITUTE

Dane A. Boysen, PhD
(626) 676-0410
dane.boysen@gastechnology.org